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Magnetism in V-doped ZnO thin films

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Abstract
Ferromagnetism at room temperature, along with a spin-glass-like behaviour at low temperatures, has been observed in laser ablated V-doped ZnO thin films. It is found that V atoms were well substituted for Zn atoms and resulted in a very uniform distribution among the ZnO matrices.

There has been an ongoing search for ferromagnetic semiconductors with a Curie temperature (T_C) well above room temperature which could be used for spintronics applications. One of the most recent interests is the quest for high T_C ferromagnetism (FM) in oxides such as ZnO doped with Co [1], TiO_2 doped with Co, [2, 3] Fe, [4, 5] Ni [5] or V [6], and SnO_2 doped with Co [7] or Fe [8].

Besides the search for materials with a high T_C along with large magnetic moment, it is very important to find doped compounds which have good homogeneity; in other words, the dopants can be well dissolved and the dopant atoms are distributed uniformly among the host matrices.

Theoretical calculations predicted that doping V may induce FM in semiconducting oxides [9], but so far, not much work has been done in this direction. V-doped TiO_2 thin films are room temperature ferromagnets with a very large magnetic moment [6], while V:ZnO films might be ferromagnetic but only when the films were conductive [10]. (Note that, in fact, in this work, V:ZnO films were deposited on top of a 5 nm-thick-layer of ZnO; therefore, the properties are not those of V:ZnO monolayers [10].) In this paper, we undertook a study of the magnetism of V-doped ZnO thin films.

A $Zn_{0.95}V_{0.05}O$ target was made by a sol–gel method. 200 nm-thick V:ZnO films were grown by the pulsed laser deposition (PLD) technique using a KrF laser ($\lambda = 248$ nm) on R-cut sapphire ($1\bar{1}02$) substrates. The repetition rate was 3 Hz and the energy density was 2 J cm^{-2}. The substrate temperature was 600, 650 or 700 °C. During deposition, the oxygen partial pressure (P_{O_2}) was kept as 10^{-1} Torr, and after deposition, the films were cooled down slowly to room temperature under a P_{O_2} of 300 mTorr. The structural study was done by x-ray

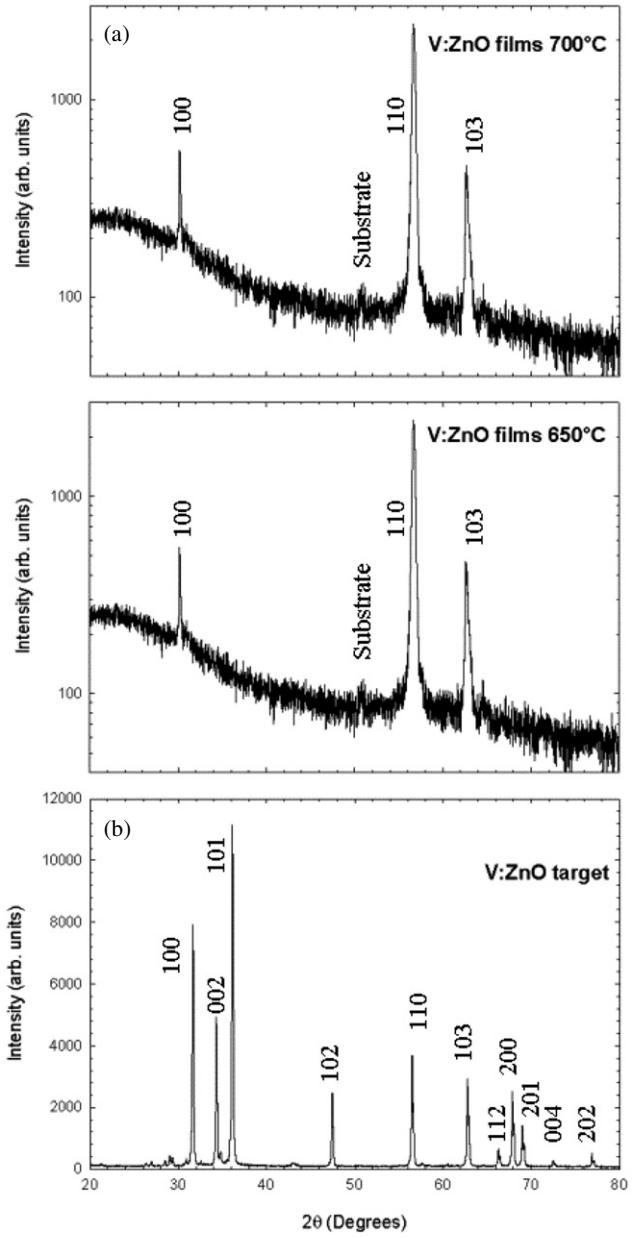

Figure 1. X-ray diffraction patterns of (a) V-doped ZnO films fabricated at 650 and 700 °C and (b) the $Zn_{0.95}V_{0.05}O$ target.

diffraction (XRD). The resistances of all samples were measured by the two-probe method using a resistance-meter. The magnetization measurements were performed by a quantum design superconducting quantum interference device (SQUID) system from 0 up to 0.5 T under a range of temperatures from 400 K down to 5 K. The chemical compositions were determined by the Rutherford backscattering spectroscopy (RBS) method whose parameters have been mentioned elsewhere [5].

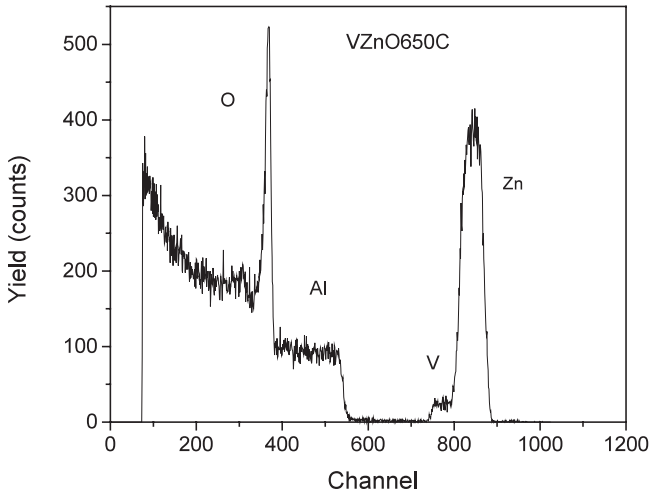

Figure 2. RBS spectra of the V-doped ZnO films fabricated at 650 °C.

As is seen from XRD pattern of the V:ZnO target shown in figure 1, the target is single-phased hexagonal wurtzite; no impurity peak is found and the films are well crystallized with only three very sharp peaks of wurtzite structure appearing (spectra shown in log scale did not show any secondary phase; also, note the high intensity of the peaks). It seems that the V was dissolved well into the ZnO structure. The V content in V:ZnO films is determined from RBS data to be 12.87%, 11.11% and 8.36% for films fabricated at 600, 650 and 700 °C, respectively.

All of our V:ZnO films are semiconductors with a resistivity at room temperature of about 1.5 Ω cm which increases rapidly when the temperature decreases. This value is comparable to what was reported by Matsumoto *et al* for Co-doped TiO_2 [2]. This is worth noting, because if the FM that we found is not associated with the semiconductivity, it would be evidence for V remaining as metal clusters, as in the case of V:ZnO films [10] or Co:TiO_2 films, [11] in which the FM observed resulted from the formation of dopant clusters, causing them therefore to be metallic at room temperature.

The RBS spectra showed that both Zn atoms and V atoms are distributed very uniformly in the films. As is seen from figure 2, the peaks of Zn and V are well separated, indicating that the determinations of Zn and V contents in the films could be rather precise (when there is an overlapping, it is not possible to say definitely what the number of atoms of each element is). The V peak has a similar rectangular shape to that of the Zn peak, showing that the V distribution in the V-doped ZnO films is very uniform over the whole thickness of the film (the same result is found from detailed simulations for the ratio of V and Zn in each layer). It is completely different from what were found in Co/Fe/Ni-doped TiO_2 film [12, 13] and Co-doped ZnO film, [14] where the dopant atoms were localized mostly in the layer of 40 nm taken from the surface. And it reveals that compared to Co, V is not any more difficultly dissolved into ZnO, and it is different from what Jin *et al* reported, namely that Cr, Mn, Fe and Co are the most soluble among all the elements of the transition-metal group [15]. Thus, we must say that not only does the nature of dopant decide whether its distribution is uniform or not, but the distribution must also depend very much on the growth conditions.

V:ZnO films fabricated at either 600 or 650 °C are ferromagnetic at room temperature (see figures 3 and 4). However, the saturation magnetization (M_s) of the films fabricated at 650 °C is one order of magnitude larger than that of films grown at 600 °C. The maximum value of

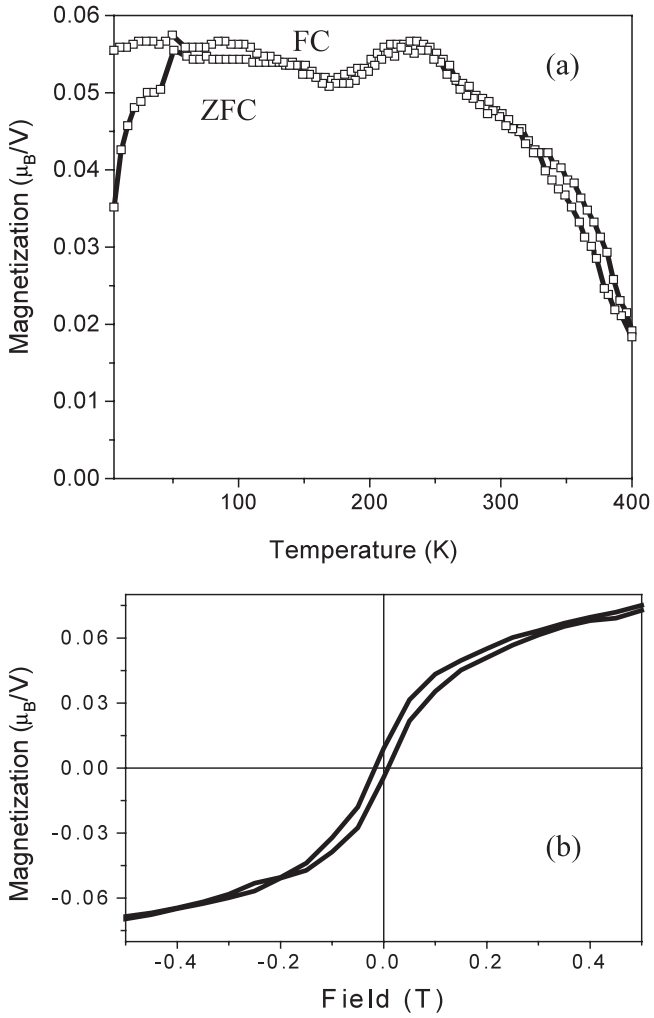

Figure 3. Magnetization of a V-doped film fabricated at 600 °C (a) versus temperature measured at ZFC and FC of 0.2 T and (b) versus magnetic field at 10 K.

M_s we could obtain in V:ZnO films is 0.6 μ_B/V. This value is rather modest, and it is much smaller than the value as of 4.2 μ_B/V obtained in V:TiO_2 films [6]. As is seen in the $M(T)$ curve, there is a shoulder at about 220 K, indicating that in the film there are some minor parts which partially tend to be antiferromagnetic, but the majority certainly remains ferromagnetic, and such a ferromagnetic phase is still strongly dominant over the whole range of temperatures. Even though the M_s value is small, the films are clearly room temperature ferromagnetic, as evidenced from the value of T_C higher than 400 K seen from figure 3(a), and from the well-defined hysteresis loops which were observed in $M(H)$ curves taken at various temperatures in the range from 10 to 300 K (see figures 3(b) and 4). At low temperatures, there is a clear discrepancy between the zero field cooled (ZFC) and field cooled (FC) temperature dependence of the magnetization, and this might indicate a spin-glass-like behaviour. It is similar to what was observed in Co-doped ZnO thin films [16, 17] and Mn-doped ZnO bulk [18], and it may be typical for transition-metal-doped ZnO. Since the isolated V atom has a magnetic moment

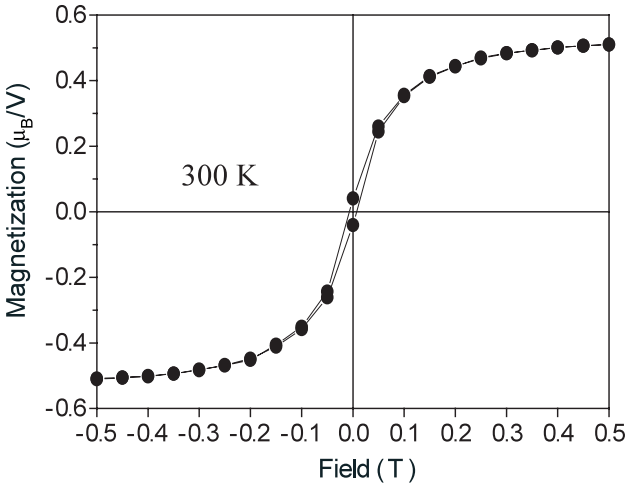

Figure 4. Magnetization versus magnetic field taken at 300 K for a V-doped ZnO film fabricated at 650 °C.

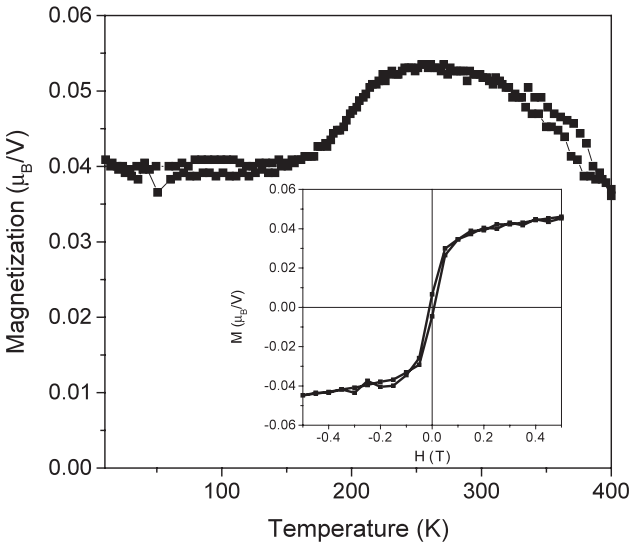

Figure 5. Magnetization versus temperature under 0.2 T for a V-doped film fabricated at 700 °C (FC and ZFC). The inset shows the $M(H)$ curve taken at 10 K.

of 3 μ_B and bulk V is paramagnetic, the value of M_s as small as 0.6 μ_B cannot come from those. Some theoretical work reported that when the V cluster is of the size of two atoms, it can give such a value [19]. But from the uniform distribution of V seen from RBS data, it is not possible to assume that the whole specimen consists of many clusters with the same size as that of two atoms and that they are distributed homogeneously in the samples (note that the number of V atoms in the film of 5×5 mm^2 is about 2.5×10^{16} atoms). Thus, it is more convincing if the magnetism we found in V:ZnO films originated from V-doped ZnO matrix. However, when the substrate temperature was increased to 700 °C, the antiferromagnetic phase which appeared slightly in the samples grown at 600 and 650 °C seems to be more prevalent below

200 K (see figure 5). Even though the $M(H)$ curve taken at 10 K (in the inset of figure 5) with a hysteresis proves that the sample is still weakly ferromagnetic at low temperatures, the $M(T)$ curve confirms the existence of the antiferromagnetic phase ($T_{\text{Neel}} \approx 200$ K). This may indicate that, at higher temperatures, there are more dopant–dopant associations which make the magnetic moment decrease and that there may be some possibility for precipitations (the magnetic moment of a V cluster of a size bigger than 15 atoms can give a value of about 0.03 μ_B) [19][3].

In conclusion, V-doped ZnO thin films grown at 600–650 °C by laser ablation on sapphire substrates show room temperature ferromagnetism along with a spin-glass-like behaviour at low temperatures. It is found that the V atoms were well substituted for Zn atoms and that they were distributed very uniformly in the ZnO matrix. Different growth conditions could result in different values of saturation magnetic moment and an increase of the substrate temperature above 650 °C seems to favour a secondary phase which is antiferromagnetic.

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[3] The RBS data for the sample fabricated at 700 °C showed more fluctuations in the ratio of V compared to those fabricated at 600 and 650 °C and it may be related to some precipitations.